Determination of the parameters of crystallization of maleic anhydride modified polypropylene in model composites with glass fibres

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Abstract— **Isothermal and nonisothermal crystallizations of maleic anhydride-modified iPP in glass fibres model composites with unsized and sized glass fibres were studied by differential scanning calorimetry (DSC), to evaluate the influence of glass fibres on crystallization behavior. Isothermal crystallization was followed in the temperature range from 391 K to 403 K, and the rate constant and Avrami exponents were determined. Nonisothermal crystallization was carried out at different cooling rates (1 -20 K/min). It was found that the crystallization kinetics of MAH-iPP was significantly altered in model composites. Decreased energy of formation of a nucleus with critical dimensions and decreased activation energy for nonisothermal crystallization were determined for the model composites with sized glass fibres, indicating faster growth of lamellae, in spite of model composite with unsized glass fibres.**

Keywords- Isotactic polypropylene; maleic anhydride modified iPP; crystallization; isothermal; nonisothermal; glass fibre composites

I. INTRODUCTION

Chemical modification of iPP by grafting of different monomers gives opportunities for introducing of the monomers in the polymer chain, without altering basic characteristics of the polymers. Grafting of acrylic and metacrylic acid, acrylamide, ethylene glycol, methacrylate, maleic anhydride, etc. is described in many articles [1-7]. Maleic anhydride modified iPP contains polar carboxylic groups, which influences the adhesive properties and interfacial bonding strength between the polymer matrix and the reinforcements in fiber reinforced composites [8].

In our previous work crystallization of homo- iPP in model composites with glass fibres thermally treated and fibres containing different sizings was investigated. It was found that the glass fibres are week α-nucleators and they rise the nucleation density insignificantly [9-11].

In this work we examine the influence of the fiber surfaces with different character on crystallization of maleic anhydride modified iPP containing polar carboxylic group. We have determined the basic parameters of crystallization of model iPP based composites with glass fibres, with and without thermoplastic compatible sizing. Based on the Kissinger method, the activation energy for crystallization has been calculated for model systems with differently treated glass fibers.

II. EXPERIMENTAL

Isotactioc polypropylene i**PP** with a melting flow index, MFI of 36 g/10 min and maleic anhydride modified iPP, MAH modifier (Polybond 3150), with MFI of 50 g/10 mm, and a grafting degree of 0.5 % MAH, were used. The procedure for obtaining the modified iPP (MPP) was previously published [8].

Model composites MPP/glass-fibers were prepared with 60 wt% glass fibers (GF), sized with and without thermoplastics compatible sizing. Amount of glass fibres in the investigated model composites is equal to those used in real iPP based composites. Assignation of model composites is given in Table I.

Isothermal and nonisothermal crystallization of the samples were analyzed by DSC. In isothermal regime, the sample was rapidly heated to 478 K and held in the molten state for 5 min, to erase the thermal history of the polymer. Then the sample was cooled to a given crystallization temperature, T_c with a cooling rate of 80 K/min. Isothermal crystallization was carried out at T_c until crystallization was completed

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Table I. Assignation and of the composite samples

assignation	**content**
MPP	Maleic anhydride modified iPP
CMPS	MPP + 60 wt% silane sized glass fibres
CMPU	MPP + 60 wt% urethane sized glass fibres
CMPG	MPP + 60 wt% unsized glass fibres

The crystallization under nonisothermal conditions was performed by cooling at different cooling rates: 1, 3, 5, 10, 15 and 20 K/min. The experiments were carried out with a Perkin Elmer DSC-7 analyzer under nitrogen and the calibration was performed with indium and zinc. The sample weight in all experiments was 7.0 mg. Based on the determined values for the enthalpy of crystallization, the crystal conversion, α, is calculated by equation (1).

$$\alpha = \frac{\int_0^t \left(\frac{dH}{dt}\right) dt}{\int_0^\infty \left(\frac{dH}{dt}\right) dt} = f(t) \qquad (1)$$

From the obtained $\alpha = f(t)$ curves, of the induction time (t_i), as well as the half-time of crystallization ($t_{0.5}$) were determined. [12]

III. RESULTS AND DISSCUSION

Curves of the crystal transformation (Figure 1) show that the crystallization of iPP in these systems is in accordance with the kinetic theory of crystallization, and the rate of crystallization decreases with increasing of T_c. Glass fibres affect the crystallization of MPP. The highest rate of the crystal transformation is seen for the composite containing glass fibres with silane sizing , and the lowest - for composite with unsized untreated glass fibres.

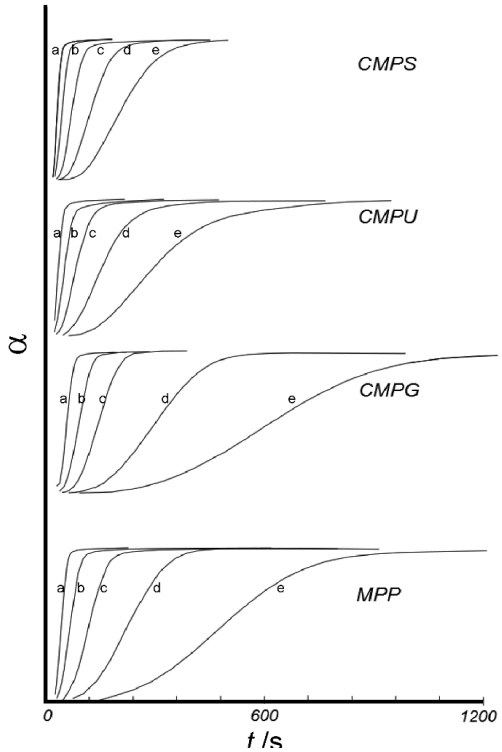

Figure 1. Crystallization curves of MPP and composites at different T_c (K): (a) 397; (b) 400; (c) 403; (d) 406; (e) 409.

The dependence of the half time of crystalization ($t_{0.5}$) on the temperature of crystallization is shown on Fig.2. The half time of crystallization in model composite with silane sizing (CMPS) is 243 seconds, while for MPP $t_{0.5}$ is 474 seconds (at temperature of 403 K); for the composite with unsized fibres $t_{0.5}$ is 587 seconds.

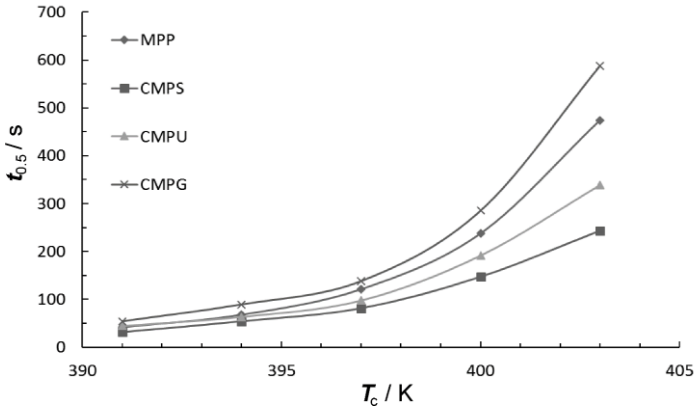

Figure 2. Dependence of the half-time of crystallization ($t_{0.5}$) for MPP and MPP/GF composites on T_c.

As evidenced from Figure 3, the plot log (-ln (1 - α)) versus log (t) yields a straight line, indicating that the kinetics of crystallization follows the application of Avrami equation [13]:

$$\alpha = 1 - \exp(-kt^n) \qquad (2)$$

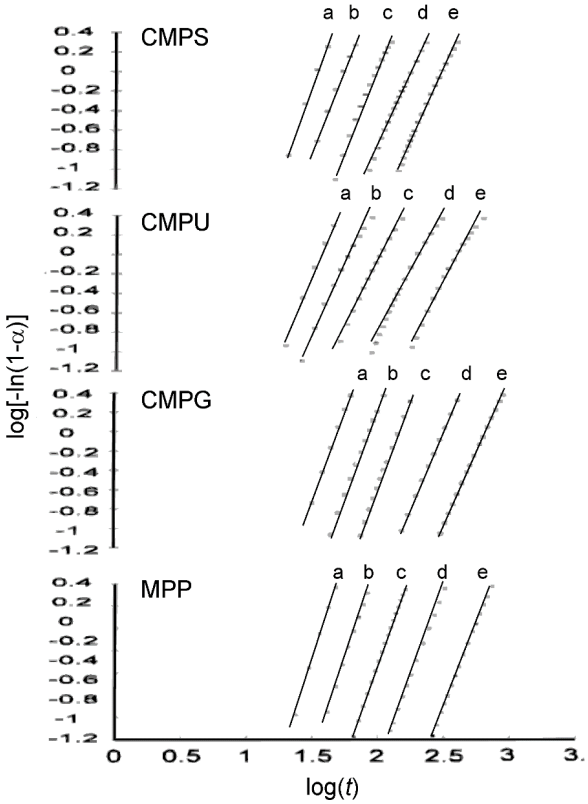

Figure 3. Avrami plots of MPP and MPP/GF composites at different T_c (K): (a) 397; (b) 400; (c) 403; (d) 406; (e) 409.

The Avrami exponents n were determined, and a tendency of decreasing values of n with increasing T_c is found in the investigated interval of T_c (Figure 4).

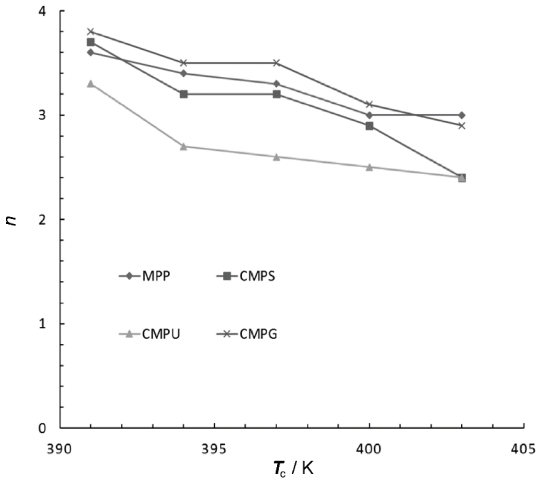

Figure 4. Dependence of the Avrami exponent, n on the temperature of crystallization, T_c.

The rate of crystallization depends on the creation of nuclei from which the crystal growth starts (primary nucleation),. In the case of polymers this rate depends also on the secondary nucleation that is initiated on the lamellae surface.

Primary nucleation can be heterogeneous, in the presence of some additives/nucleators, and homogenous, when nucleuses are created from the polymer melt by thermal fluctuations. Additives often represent heterogeneous nucleuses from which polymer crystals grow, and this process does not depend on the temperature, opposite to homogenous nucleation which is a temperature dependent process.

Avrami coefficients depend on the type of nucleation, and in the case of heterogeneous nucleation n is usually lower compared to homogenous nucleation. It is seen that for CMPS and CMPU the values of n are lower compared to the neat polymer, MPP and to the CMPG system, and this is valid for all crystallization temperatures. It should be noted that the values of the Avrami coefficients for CMPG are higher than the ones of the neat polymer.

For the systems in which heterogeneous nucleation is favored, isothermal crystallization starts earlier and the induction period (t_i) is shorter. In the case of nonisothermal crystallization, the crystallization peak temperature is higher compared to neat polymer. The induction period for crystallization, t_i is determined from the curves given in Figure 1, and the dependence of t_i on T_c is given on Figure 5.

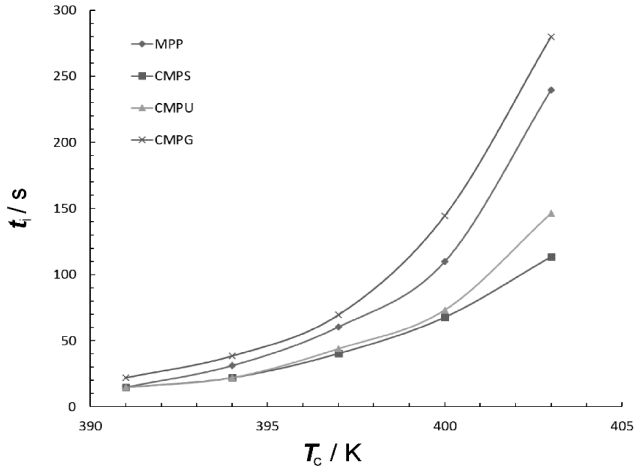

Figure 5. Dependence of the induction time, t_i for MPP and MPP/GF composites on T_c.

Glass fibers are week nucleators and usually the nucleation of iPP in their presence is a only insignificantly favored [9-11]. In model composites with sized glass fibers the crystallization starts earlier compared to the neat polymer at all temperatures of crystallization. Crystallization in model composite with unsized glass fibres started

later compared to MPP, which indicates on the decreased nucleation, related to maleinated polymer. This observation is in line with the higher values of *n* determined *for* this system.

The results of non isothermal crystallization are supplementary with those from isothermal. The values of the crystallization peak temperatures are moved to the higher values for CMPU and CMPS, while T_p of the CMPG is located at lower temperatures related to MPP (Figure 6).

This is probably due to the influence of the polar groups of maleic anhydride, grafted on the polymer chain, responsible for the interactions with the sizings components on surface of the glass fiber.

One of the theories of adhesion is based on the acid-base interactions [14]. The examination of the surface of the glass fibbers has shown that the surface of unsized fibers exhibits acidic character, while the silanesized surface has base character and polyurethane sized glass surface are amphoteric [15, 16].

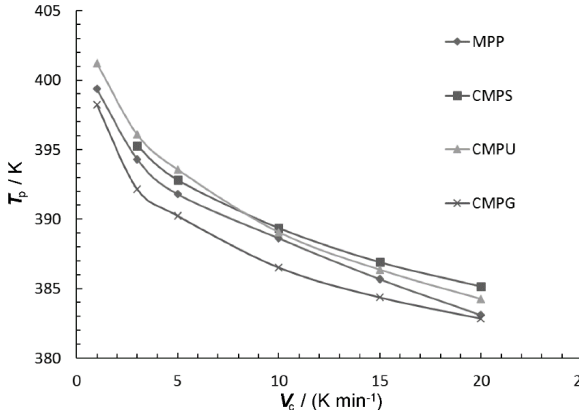

Figure 6. Dependence of the maximum at crystallization peak, T_p for MPP and model composites crystallized at different cooling rates, V_c.

It is known that acid-base interactions at the contact polymer/fibers can drastically increase the interfacial adhesion, and the wetting of the fibers with polymer melt is enhanced in the stage before crystallization starts, because the compatibility between the components is improved. These phenomena are probably connected with the nucleation of the polymer on the fibers surface already in the phase of cooling the polymer melt, which is stimulated by the establishing chemical links between the carboxylic groups of maleic anhydride and NH_2 groups of polyurethane or amine-containing sizing. These are most probably the reasons why the sized glass fibers increase nucleation density and silane sized glass fibers with base character has highest nucleation density. "Amphoteric" glass fiber surface exhibit lower nucleation efficiency.

Growth of the polymer crystals depend on the secondary nucleation, actually on the energy for forming of secondary nucleus. For calculations of this parameter we used the half-time of crystallization, $t_{0.5}$ which is connected to the kinetics parameters of the process given by the equation:

$$k = \frac{ln2}{t_{0.5}^{n}} \qquad (3)$$

According to the kinetic theory of polymer crystallization [17], assuming that the growth of lamellae is controlled by a process of secondary nucleation, the temperature dependence of the overall kinetic constant, *k*, is given by the relation (6):

$$\frac{\log(k)}{n} = A_0 - \frac{\Delta F^*}{2.3RT_c} - \frac{\Delta \Phi^*}{2.3KT_c} \qquad (4)$$

where A_0 is a constant (assuming that the primary nucleation density at each T_c, does not vary with time), ΔF^* is the activation energy for the transport of crystallizing units across the liquid/solid interface, *K* is the Boltzmann constant, *n* is the Avrami exponent, and $\Delta \Phi^*$is the energy of formation of a nucleus with critical dimensions.

Dependencies given on Figure 8 are linear, and applying the equation 2, energies for forming secondary nucleus, $\Delta \Phi^*$ are calculated; the lower value indicates better secondary nucleation and faster lamellae growth.

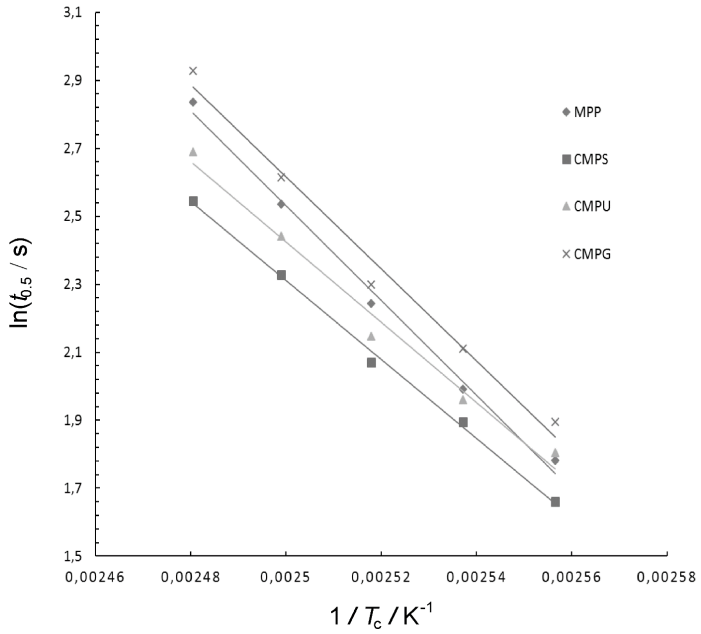

Figure 7. Dependence of log($t_{0.5}$) on 1/T_c.

The lowest energies for forming secondary nucleus, $\Delta\Phi^*$and best conditions for secondary nucleation has composite with silane sizing and the worse, the composite with unsized glass fiber. (Fig. 8).

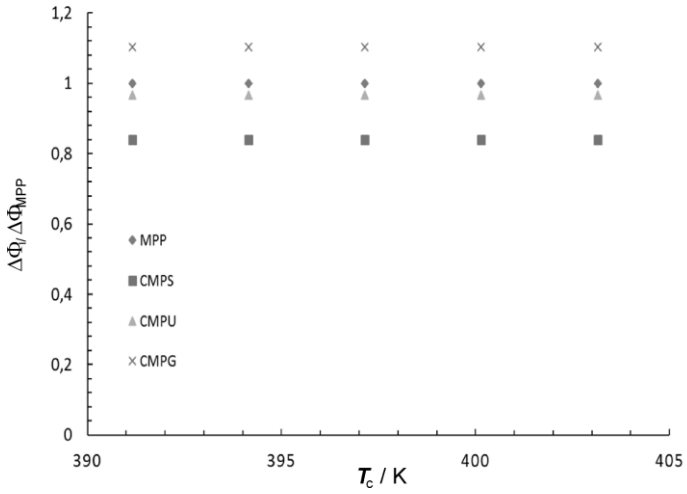

Figure 8. Ratios of the energy of formation of nucleus of critical dimensions versus crystallization temperatures, T_c.

The activation energy for crystallization, ΔE (dynamic factor characterizing the process of transport of macromolecular segments to the surface of crystal growth) can be calculated from the crystallization peak temperature ,T_p and the heating rate, V_c, using the Kissinger equation [18]:

$$\frac{d[\ln(\frac{V_c}{T_p^2})]}{(\frac{1}{T_p})} = \frac{-\Delta E}{R} \qquad (5)$$

where R is the universal gas constant. The activation energy of nonisothermal crystallization of MPP and its composites are easily calculated from the slope of the curves plotting ln (V_c/T^2_p) versus $1/T_p$, as shown on Figure 9.

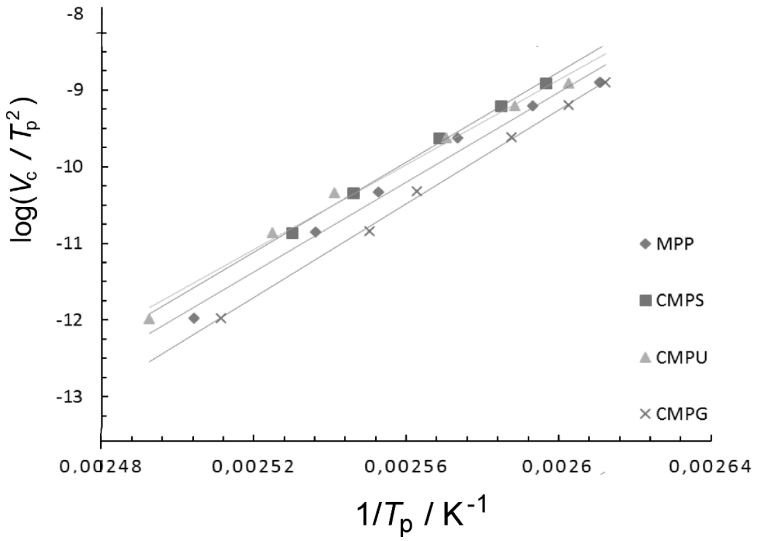

Figure 9. Kissinger plot for MPP and MPP/GF model composites.

The ΔE value of MPP is 244.3 kJ/mol, and the values for composites with sized glass fibres are 244.2, and 229.7 kJ/mol for CMPG and CMPU, respectively. The value for activation energy for composite with unsized fibres is 255.5 kJ/mol and it is higher than MPP. Lower activation energy for composites with sized glass fibres indicate on relieved crystallization behavior compared to MPP.

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IV. CONCLUSIONS

The presence of reinforcing fibers can alter the crystallization behavior and the morphology of the polymer matrix, affecting the overall composites properties. In this work we examined the model composite systems containing polypropyloene as a matrix and glass fibers as commonly used reinforcement for thertmoplastics based composite materials. It was shown that the crystallization behavior of maleic anhydride modified iPP (MPP) was altered by the presence of differently sized glass fibers in model composites. The presence of sized glass fibres has resulted in a decreased energy of formation of nucleus with critical dimensions and improved conditions for secondary nucleation. As a consequence, the rate of crystal conversion was increased compared to the neat polymer, MPP. The Avrami coefficients exhibited lower values for the model composites containing sized glass fibers at all investigated crystallization temperatures, due to the promoted heterogeneous nucleation in these systems. Higher nucleation for nonisothermal crystallization resulted in shifting of the crystallization peak temperature toward higher values due to the presence of silane and urethane sized fibers, in spite to unsized ones, pointing out the influence of glass fibre surface on the overall parameters of polymer crystallization. Our further work will be focused on examination of the mechanical properties of bulk composite materials containing differently treated and sized glass fibers and MPP.

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